THE DETERMINATION OF THE COMPOSITION OF THE MnO_2—Mn_2O_3—Mn_3O_4 SYSTEMS

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INTRODUCTION

Many investigators have dealt with the thermal behaviour, structure and modifications of the different manganese oxides. Extensive data is also available in the literature concerning the microscopical examinations of the oxidized manganese minerals.

However, little attention has been focussed to develop a simple method for the simultaneous determination of the different oxide components. A method is required by means of which based on chemical analytical data the proportion of the oxide components in an artifical mixture, or in natural ore complex can not only be approximately estimated but exactly determined. Such a method is not so useful for analytical purposes, but rather for the geochemistry of the manganese ore deposites furnishing useful data from the point of view of the genesis of the different manganese ores.

So far, in the course of the chemical analysis the total manganese content was determined and given in terms of MnO, the active oxygen amount was also determined thus the final result of the analysis was given in terms of MnO and O. The second method used recalculates first the total manganese content determined by means of the Volhard-Wolff method to MnO_2 and then determines the actual MnO_2 content too by means of the oxalate or ferrous-sulphate methods. The latter amount is subtracted for the total manganese content also given in terms of MnO_2 and the difference calculated to MnO. Thus in the final results of the analysis in this case MnO_2 and MnO are given. In the different papers the analytical data relating to the oxidized manganese ores the composition is indeed given in terms of MnO and O or MnO_2 and MnO.

Concerning the determination of the active oxygen content (MnO_2 content) it should be noted that the presence of ferrous iron interferes with the determination, both in the case of the oxalate method and in that of the ferrous sulphate one. Ferric iron does not interfere. In the presence of FeO an MnO_2 determination will be low in proportion to the amount of FeO present. Once the FeO content exceeds the MnO_2, then it is

impossible to determine MnO_2 (active oxygen) chemically. The most that can be done when MnO_2 is in excess of FeO is to determine the excess.

It is possible that in many cases these data are sufficient for the chemist as he knows the effect value of the oxidized manganese ore through the determination of the active oxigen. However, the mineralogist is always also interested in the mineral composition of the ore complex as from the geochemical genetical point of view this is very essential. Thus he attempts to establish from the above data through calculation and/or microscopic examinations what kind of, and mainly what amounts of manganese oxide the materials investigated contains. The determination described below is designed to substitute these calculations by an exact method which enables the determination of the composition of the MnO_2-Mn_2O_3-Mn_3O_4 systems — taking the most frequent components into consideration — merely on the basis of the data of the chemical analysis.

THE POSSIBILITY OF DETERMINATING THE COMPOSITION MERELY ON THE BASIS OF THE MnO_2—MnO OR MnO—O VALUES.

It was mentioned above that the mineralogist had to carry out calculations even if he possessed analytical data and if he also supplemented these calculations with microscopical examinations he could after all not obtain quite precise results. There are, of course, simple cases when the quality of the manganese ore can be unequivocally determined on the basis of the above data.

For example on dealing with the material of the Hungarian manganese ore occurences those occuring at Regéc were also investigated. The total manganese content expressed in terms of MnO_2 determined by means of the Volhard-Wolff procedure was 15,19 per cent and that determined with the oxalate procedure was 15,39 per cent. A similar result was obtained on examining the substance of the occurence of Mád. On estimating the total manganese content and returning it as MnO_2 or by determining the amount of the MnO_2 actually present with the oxalate procedure the MnO_2 content of the material was always 37,7 per cent.

Hence the correspondence within error limits of the MnO_2 content determined by means of different procedures points to the fact that in the above and similar cases the presence of pure pyrolusite may be taken into account.

There are, however, also more complex cases in which the MnO_2—MnO or MnO—O values, respectively, are perhaps enough for the evaluation of a manganese ore from the industrial point of view, but are not sufficient for the determination of the exact mineral composition, the estimation of the proportion of the single components. For each given MnO—O or the corresponding MnO_2—MnO values, respectively, in the presence of two components (MnO_2—Mn_2O_3, MnO_2—Mn_3O_4, Mn_2O_3—Mn_3O_4) — with the exception of two values — there may be in all cases two different possible composition, or in the presence of three component a whole sequence of possible compositions.

The two exceptional cases mentioned above are:

a) MnO_2 = per cent and MnO = 0,00 per cent or corresponding to it respectively, MnO = 81,59 per cent and O = 18,41 per cent. In the case of these values only MnO_2 is present.

b) MnO_2 = 37,99 per cent and MnO = 62,01 per cent or corresponding to it, respectively, MnO = 93,01 per cent and O = 6,99 per cent. In this case only Mn_3O_4 may be present. (Fig. 1.)

These two extreme MnO_2—MnO or MnO—O values, respectively, may be considered as two limit values, thus between them each pair may have two binary and a whole sequence of ternary systems varying in composition.

For example: MnO_2 = 50,00 per cent and MnO = 50,00 per cent, or corresponding to it MnO = 90,80 per cent and O = 9,20 per cent. Hence in the case of two components the composition of the two possible systems is:

	MnO_2 %	MnO %	MnO %	O %
20 % MnO_2 + 80 % Mn_3O_4	50,4	49,6	90,73	9,27
71 % Mn_2O_3 + 29 % Mn_3O_4	50,07	49,93	90,78	9,22

On the contrary besides these values a whole sequence of ternary systems are possible. Only to mention some examples:

Table 1.

Composition	MnO_2	MnO	MnO	O
	weight per cent			
66 % Mn_3O_4	25,08	40,92	61,39	4,61
20 % Mn_2O_3	11,00	9,00	17,98	2,02
14 % MnO_2	14,00	0,00	11,43	2,57
100 % mixture	50,08	49,92	90,80	9,20
45 % Mn_3O_4	17,10	27,90	41,86	3,14
50 % Mn_2O_3	27,50	22,50	44,93	5,07
5 % MnO_2	5,00	0,00	4,08	0,92
100 % mixture	49,60	50,40	90,87	9,13
37 % Mn_3O_4	14,06	22,94	34,42	2,58
60 % Mn_2O_3	33,00	27,00	53,92	6,08
3 % MnO_2	3,00	0,00	2,45	0,55
100 % mixture	50,06	49,94	90,79	9,21
73 % Mn_3O_4	27,74	45,26	67,90	5,10
10 % Mn_2O_3	5,50	4,50	8,99	1,01
17 % MnO_2	17,00	0,00	13,83	3,12
100 % mixture	50,24	49,76	90,77	9,23

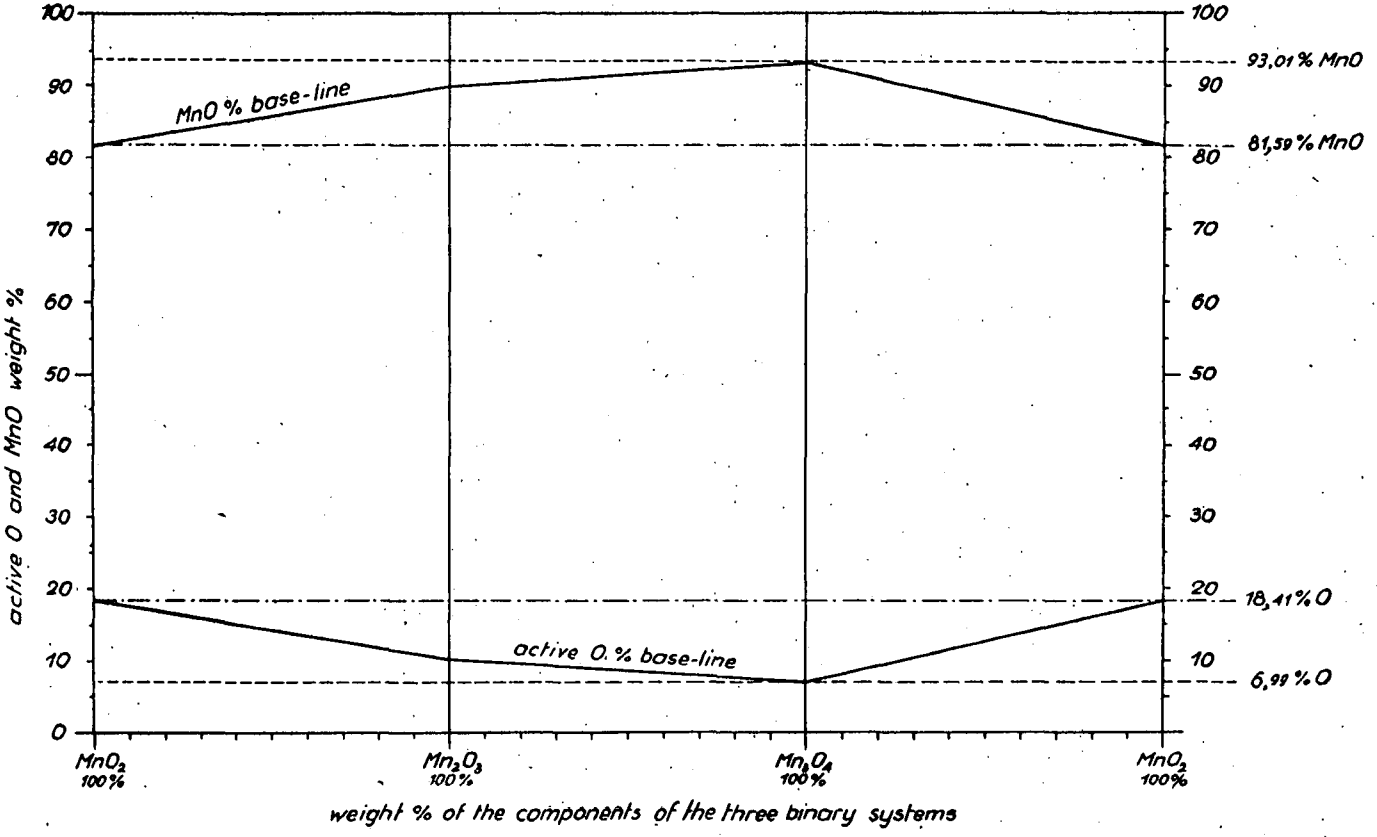
100
90
80
70
60
50
40
30
20
10
0
MnO % base-line
active O. % base-line
93,01 % MnO
81,59 % MnO
18,41 % O
6,99 % O
active O and MnO weight %
MnO2 100%
Mn2O3 100%
Mn3O4 100%
MnO2 100%
weight % of the components of the three binary systems

Fig. 1.

It is not necessary to continue the enumeration of ternary systems varying in composition and containing in equal amounts 50 per cent MnO_2 and 50 per cent MnO or correspondingly 90,8 per cent MnO and 9,20 per cent O, respectively. (In Table 1. the minimal numeral deviations from the assumed MnO_2—MnO and MnO-O values in the composition of the various mixtures are due to the fact that in the mixtures the percentages of the oxides was rounded up.)

The following Table 2. shows what kind of composition the binary systems have which correspond to the different MnO_2—MnO and the corresponding MnO—O values, respectively. (Of course not a total survey is given, but only the composition of the binary systems which can be read on Fig. 2. belonging to the values calculated per 5 per cent of the MnO_2 content.)

The MnO_2—MnO content of the systems composed of MnO_2—Mn_2O_3—Mn_3O_4 which were investigated can only vary between value limits of 100 per cent — 0 per cent and 38 per cent — 62 per cent or correspondingly those of its MnO—O content between 81,59 per cent — 18,41 per cent and 93,01 per cent — 6,99 per cent. This holds good if the system has two or three components, or even only contained one of the mentioned oxides.

The composition of the three oxides is usually represented in terms of MnO_2—MnO or MnO—O values. The theoretical values calculated on the base of the formula are as follows:

	MnO_2 — MnO		MnO — O	
MnO_2	100,00	— 0,00	81,59	— 18,41
Mn_2O_3	55,06	44,94	89,86	10,14
Mn_3O_4	37,99	62,01	93,01	6,99

The use of the MnO—O values for all three oxides to express the composition is unequivocal and correct, but the same does not hold good to the same extent if the composition is expressed in MnO_2—MnO values. Namely whilst Mn_3O_4 can be considered to be $Mn^{2+}Mn^{4+}O_4$ and also as $Mn^{2+}_2Mn^{3+}_2O_4$ on the other hand, the expression of Mn_2O_3 as MnO. MnO_2 i. e. $Mn^{2+}Mn^{4+}O_2$ cannot be considered as logical, considering that Mn_2O_3 contains trivalent and not divalent and tetravalent manganese. (Besides, the question as to whether the manganite only contains trivalent manganese or di- and tetravalent one is not yet settled decisively.) In the following only the MnO—O values will be used as with these the composition of all oxides can be logically represented.

As can be seen from the above data with the exception of the two cases mentioned the exact establishment of the composition, merely on the basis of the MnO—O values, is not even possible if it is sure that only two of the three components are present, but becomes impossible in the presence of all three components. Hence for the unequivocal definition of the composition still one factor is required. Therefore, the thermal behaviour of the oxides in question will be dealt with brifely.

Table 2.

MnO_2 — MnO		MnO — O		The composition of both possible binary systems expressed in weight per cents			
weight per cents							
100	0	81,59	18,41	MnO_2	100	———	
95	5	82,51	17,49	MnO_2 Mn_2O_3	89 11	MnO_2 Mn_3O_4	92 8
90	10	83,43	16,57	MnO_2 Mn_2O_3	78 22	MnO_2 Mn_3O_4	84 16
85	15	84,35	15,65	MnO_2 Mn_2O_3	66 34	MnO_2 Mn_3O_4	76 24
80	20	85,27	14,73	MnO_2 Mn_2O_3	55 45	MnO_2 Mn_3O_4	68 32
75	25	86,19	13,81	MnO_2 Mn_2O_3	44 56	MnO_2 Mn_3O_4	60 40
70	30	87,11	12,89	MnO_2 Mn_2O_3	33 67	MnO_2 Mn_3O_4	52 48
65	35	88,03	11,97	MnO_2 Mn_2O_3	22 78	MnO_2 Mn_3O_4	44 56
60	40	88,95	11,05	MnO_2 Mn_2O_3	11 89	MnO_2 Mn_3O_4	36 64
55	45	89,86	10,14	Mn_2O_3	100	MnO_2 Mn_3O_4	28 72
50	50	90,80	9,20	Mn_2O_3 Mn_3O_4	71 29	MnO_2 Mn_3O_4	20 80
45	55	91,72	8,23	Mn_2O_3 Mn_3O_4	59 41	MnO_2 Mn_3O_4	12 88
40	60	92,64	7,36	Mn_2O_3 Mn_3O_4	11 89	MnO_2 Mn_3O_4	4 96
38	62	93,01	6,99	Mn_3O_4	100	———	

THE LOSS ON IGNITION, OR THE ACTIVE OXYGEN CONTENT AS FACTORS OF THE DETERMINATION OF THE COMPOSITION

At high temperatures the most stable oxide of manganese is Mn_3O_4. If manganese oxides are heated in air at 1000° C all are converted to Mn_3O_4. Thus the sample examined contains only Mn_3O_4 then e. g. heating to 700° C there occurs no change, no loss on ignition nor any difference between the active oxygen content of the sample ignited at 700° C and between that of ordinary temperature can be observed. On the other hand, if the sample also contains some Mn_3O_4 this component does not undergo any change in the course of the heating.

According to Mason in air Mn_2O_3 is stable between temperature limits of 530—940° C. The lower temperature limit is insignificant as Mn_2O_3 if heated to temperatures below 530° C cannot be converted into another manganese oxide, however, at 900° C its conversion into Mn_3O_4 begins, as is shown by the DTA examinations. If it is heated at 700° C like Mn_3O_4 it does not undergo any change.

As contrasted with the above oxides MnO_2 heated at 550—600° C loses oxygen thus it is converted into Mn_2O_3 with a loss of weight.

$$2\ MnO_2 \xrightarrow[-O]{550—600°\ C} Mn_2O_3;\ \text{loss on ignition} = 9{,}20\ \text{per cent}$$

As in the course of heating at a temperature of 700° C of the oxides in question merely MnO_2 undergoes a change at the first approach it seems as if the loss of weight would represent a useful factor for the determination of the composition. Thus in the following it will be investigated if the value of the loss on ignition can be used for our purposes and if so between which limits.

I. On heating the sample at 700° C no loss on ignition could be observed.

a) In this case all three components cannot be present, MnO_2 will be missing, the presence of Mn_2O_3 or Mn_3O_4 or possibly some kind of mixture of the two can be seen from the determination of the MnO—O values of the sample of ordinary temperature and in the case of mixture the composition can be established on diagram N°. II. of Fig. 2. As can be seen on Table 2. this case may occur (i. e. a lack of MnO_2 simplifying essentially the estimation of the composition) if the value of MnO—O ranges between the value limits of 89,86 per cent — 10,14 per cent and 93,01 per cent — 6,99 per cent. Namely in such cases only pure Mn_2O_3 or pure Mn_3O_4 can be present, or a mixture of the two, however, the mixture containing MnO_2 are surely lacking.

b) However, the possibility that the presence of compounds oxidizing at this temperature diminishing the value of the loss on ignition must be kept in mind and it may be assumed that there occur cases when the loss on ignition caused by the possible presence of slight amounts of MnO_2 is just compensated by the increase in weight due to the oxidation of the oxidisable impurities (oxidation of ferrous iron to ferric iron). In such a

case also MnO_2 is present loss on ignition will not be observable i. e. the lack of loss on ignition must not be considered as the lack of the presence of MnO_2.

II. On heating the sample at 700° C a loss of weight could be observed.

This loss of weight, concerning natural manganese ores may be due to the following factors only taking the most frequent and essential possibilities into consideration:

a) The conversion of MnO_2 into Mn_2O_3

b) Loss of water, in the presence of clay minerals, in the case of MnOOH or some other minerals containing water

c) Loss of CO_2, in the presence of carbonates

Thus the possibilities mentioned above, b and c, increase the loss of weight due to the conversion of the MnO_2 present, which amount of the loss on ignition could be represent the measure of the quantity of MnO_2 converted. Hence a loss on ignition does not definitely point to the presence of MnO_2. If a complete analysis is available there is no special difficulty as on subtracting the determined amount of H_2O and CO_2 from the total loss on ignition the part equivalent with the MnO_2 content is obtained.

Thus essentially the two following possibilities must be taken into account:

1) The loss on ignition observed at the sample heated at 700° C can only be due to the conversion of the MnO_2 component of the ore or the artificial oxide-mixture. 2) The loss on ignition is not only caused by the conversion of the MnO_2, but other factors also play a role in its development.

In the first case — which usually only occurred with very pure natural manganese ores and principally with artificial oxide-mixtures — naturally the loss on ignition can be considered as the decisive factor for the estimation of the composition in the course of graphical plotting. In the second case if the loss of weight associated with the conversion of the MnO_2 can be precisely calculated, i. e. if it can be exactly established which other factors and in the first place to which extent played a role besides the loss of oxygen at the development of the loss on ignition, the value obtained in this manner is also useful datum for the determination of the composition. However, as can be seen these data represent more or less exact calculations.

From the above it can be established that for the estimation of the composition — besides the MnO—O value — the loss on ignition can only be considered as occasionally useful factor but not a general one.

Let us assume that it is not possible to estimate the amount of the loss on ignition which is related to the change of MnO_2 and which would be consequently in proportion to the amount of MnO_2, i. e. that we are searching for a factor substituting the loss on ignition from the value of which in every case the amount of MnO_2 may be unequivocally deduced.

This factor is the Δ O per cent representing the value of the difference of the active oxygen content of the sample of ordinary temperature and of

that heated at 700° C. With it the exact proportion of the components of the mixture can be established. The active oxygen content of the different oxides is:

MnO_2 = 18,41 per cent; Mn_2O_3 = 10,14 per cent; Mn_3O_4 = 6,99 per cent

Considering that on heating at 700° C only MnO_2 undergoes a change, the other oxides not, thus their active oxygen content also remains unchanged if one can be observed a difference between the active oxygen content of the sample of ordinary temperature and the heated one this change can only be due MnO_2 content and the measure of the change can only be proportional with the amount of MnO_2.

MnO_2	700° C	Mn_2O_3
81,59 per cent	MnO	89,86 per cent
18,41	O	10,14

$\triangle$ O = 8,27 per cent

This value can be used in all cases as it can exclusively be observed in the presence of MnO_2, other factors due not play a role in its development thus it can be unequivocally applied in the case of ores containing little amount of manganese oxides, also in presence of clay minerals, together with the MnO—O value for the determination of the composition.

THE MEASUREMENTS REQUIRED FOR THE DETERMINATION OF THE COMPOSITION AND THE GRAPHIC PLOTTING OF THE DATA.

Summarizing the above factors for the determination of the composition of an unknown mixture the following values i. e. the measurements furnishing these values are needed:

1) The total manganese content of the sample of ordinary temperature and that of one heated for three hours at a temperature of 700° C is estimated by means of the Volhard-Wolff method and expressed in terms of MnO.

2) The active oxygen content of a sample of ordinary temperature and that of heated at 700° C is determined by means of the oxalate method and expressed in terms of O.

3) The MnO—O content of the sample of ordinary temperature and that of ignited at 700° C is recalculated to 100 per cent and on the basis of these values the $\triangle$ O per cent expressing the change of the active oxygen content is calculated.

Having assesed these data they are graphically plotted thus the exact composition of artificial oxides and of pure or to a different extent contaminated natural substances containing components of MnO_2, Mn_2O_3, Mn_3O_4 can be established.

The diagram applied for the plotting is the phase-diagram of the ternary systems i. e. a prism the basis of which is formed by the triangular diagram, since it shows the composition of every possible mixture. Each side then corresponds with a binary sistem. However, it is not applied as

a space model, but laid out in the plane. Namely, the diagrams of the possible three binary systems are placed beside one another and the triangular diagram is fitted to the middle one. On the triangular diagram the amount in per cent of all three constituents can be illustrated. (Fig. 2.) Every point in the triangle represents a unique composition, respectively.

On the ordinates (I. II. III.) of the diagrams of the binary systems the theoretical MnO and O content of the pure constituents is plotted in weight per cent and the corresponding values are connected. Thus the baseline of MnO and O is obtained. Simultaneously the composition is represented by abscissae thus any proportion of the components in the diagrams of the three possible binary systems may be represented by a point on the abscissa.

The active oxygen change which MnO_2 undergoes when it is heated at 700° C and turns into Mn_2O_3 is also denoted — at the MnO_2 constituents — on the ordinates of diagrams I. and III. (For the sake of precise reading this value was denoted in a tenfold scale.) As in the case of Mn_2O_3 and in that of Mn_3O_4 the change of the active oxygen content in the course of the heating is zero the points (representing the change of the active oxygen content) plotted on the ordinates of MnO_2 are connected with the zero points of the ordinates of Mn_2O_3 and Mn_3O_4, respectively. Thus the active oxygen change, the $\triangle$ O baseline — illustrated with the dotted line — is obtained. Thus depending upon the MnO_2 content the $\triangle$ O per cent ranges in an ideal case between 0—8,27 per cent.

Therefore, on the basis of the theoretically calculated data originating from the ideal composition the diagram can be already previously prepared. Owing to this it is also necessary to recalculate to 100 per cent the data obtained at the actual determination mentioned above, enabling these data to be directly illustrated on the diagram.

In the case of binary systems if different MnO—O values (recalculated to 100 per cent) belonging together are plotted on to the ordinate and draw from these points parallels to the abscissa it can be seen that in the case of two-two components actually only two value pairs are possible as only MnO_2 or Mn_3O_4, respectively, can be present (Fig. 1.). In the case of all other MnO—O values a straigth line drawn parallel to the abscissa will always intersect on two of the three diagrams the baseline of MnO and O. On projecting these points of intersection on to the abscissa the composition of the two possible binary systems belonging to the measured MnO—O values is obtained.

In the following let us assume that the presence of all three constituents is possible i. e. let us presume that nothing is known of the composition of the sample to be examined only the data mentioned above required for the determination of the composition.

Let the result of the sample examined at room temperature be MnO = 90,8 per cent and O = 9,20 per cent. On plotting these values on diagram No. III. a composition of 20 per cent MnO_2 + 80 per cent Mn_3O_4 is obtained as the composition one of the two possible binary systems. Let us plot this composition on the corresponding side of the triangular diagram (MnO_2—Mn_3O_4) and let this be point *A'*. (Fig. 2.)

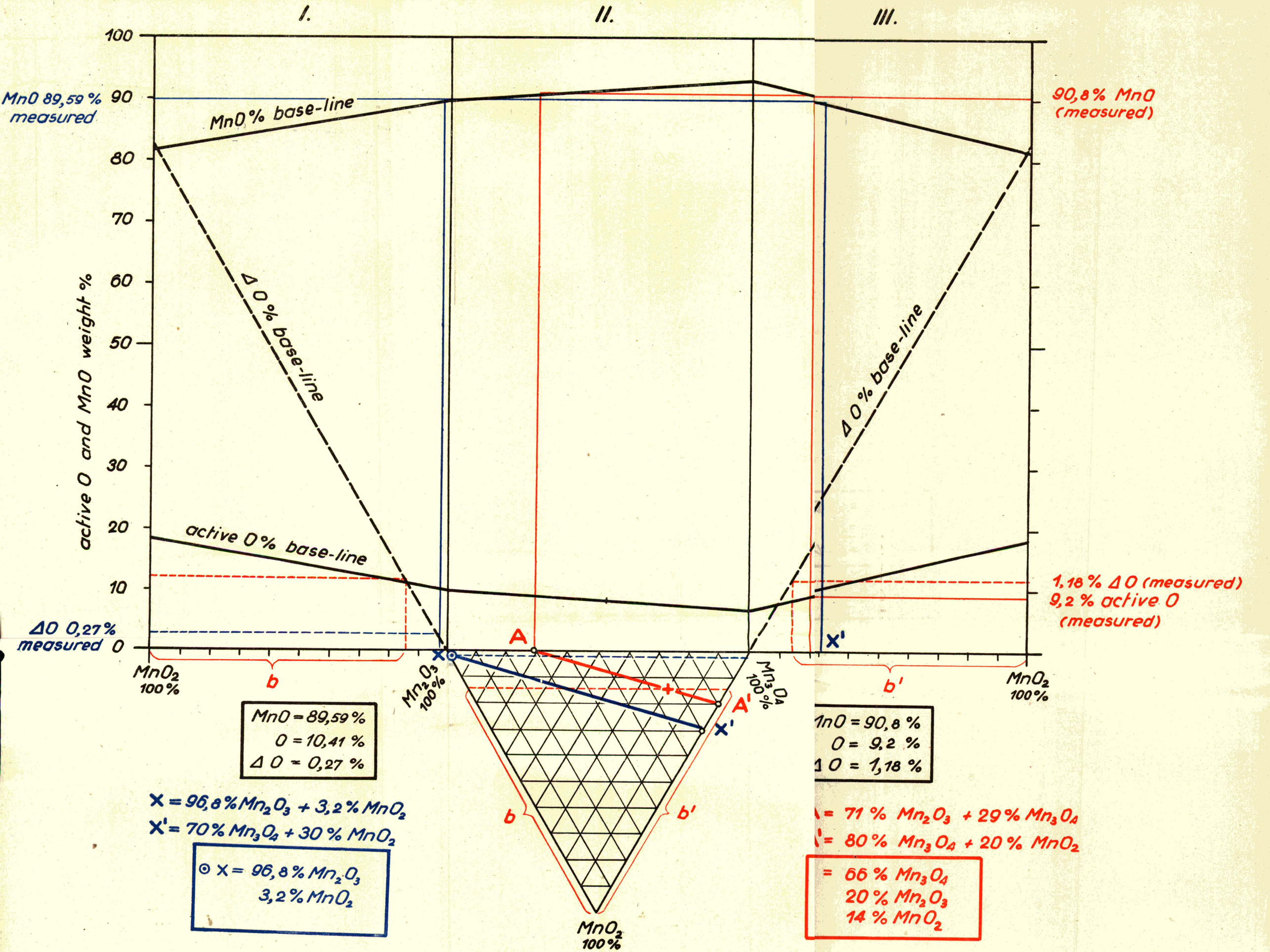
I.
II.
III.
100
90
80
70
60
50
40
30
20
10
0
MnO 89,59 % measured
MnO % base-line
Δ O % base-line
active O % base-line
ΔO 0,27% measured
90,8% MnO (measured)
1,18 % Δ O (measured)
9,2 % active O (measured)
active O and MnO weight %
MnO₂ 100%
Mn₂O₃ 100%
Mn₃O₄ 100%
b
b'
A
A'
X
X'
MnO = 89,59 %
O = 10,41 %
Δ O = 0,27 %
X = 96,8 % Mn₂O₃ + 3,2 % MnO₂
X' = 70 % Mn₃O₄ + 30 % MnO₂
⊙ X = 96,8 % Mn₂O₃
3,2 % MnO₂
MnO = 90,8 %
O = 9,2 %
Δ O = 1,18 %
= 71 % Mn₂O₃ + 29 % Mn₃O₄
' = 80 % Mn₃O₄ + 20 % MnO₂
= 66 % Mn₃O₄
20 % Mn₂O₃
14 % MnO₂

Fig. 2.

The same values on diagram No. II give the composition of the second possible binary system: 71 per cent Mn_2O_3 + 29 per cent Mn_3O_4. On the corresponding side of the triangular diagram (Mn_2O_3—Mn_3O_4) point *A* indicates this composition.

The straight line connecting points *A* and *A'* crosses all the points for which — owing to the place in the triangular diagram — corresponding ternary systems are also possible owing to the measured MnO—O values, recalculated to 100 per cent.

In the following the measure of the change of the active oxygen content decides whether we are dealing with a binary or ternary system i. e. what the proportion in per cent of the components is in the present system.

To illustrate the further course of the determination the following three examples are stated representing at the same time the three types of possibilities.

a) The values obtained at the examination of the sample heated at 700° C are: MnO = 91,98 per cent and O = 8,02 per cent. On comparing these values with the values of the sample examined at room temperature also recalculated to 100 per cent, $\triangle$ O = 1,18 per cent. A change due to heating is only possible in the case of binary systems which can be plotted on diagrams I. and III. or in the case of any ternary systems. For pure MnO_2 the value of $\triangle$ O per cent is plotted on the ordinates of diagrams I. and III. In this instance this value is 1,18 per cent, from this points straight lines are drawn parallel to the abscissa and their points of intersection at the baseline O is projected to the abscissa. The distance between the projected point and the pure MnO_2 (100 per cent) is on diagram I. *b* and on diagram III. *b'*. The two distances are always equal. The distance *b* and *b'* are plotted on the corresponding sides of the triangular diagram from the MnO_2 corner and the two end points are connected (on Fig. 2. this is designated with a dotted red line in the triangle). This straight line intersects at one point (+) the line *A*—*A'*. The locus of the point of intersection in the triangle furnishes the answer to our question: we have a ternary system the composition of which is:

66 per cent Mn_3O_4 + 20 per cent Mn_2O_3 + 14 per cent MnO_2.

b) If the values obtained in the case of the sample heated at 700° C are: MnO = 92,44 per cent and O = 7,56 per cent then on comparing the data with those of the sample of room temperature $\triangle$ O per cent amounts to 1,64 per cent.

The $\triangle$ O per cent value is plotted as previously on to the ordinate and its point of intersection with the baseline is projected on to the abscissa and the part cut off measured on the corresponding side of the triangle. On connecting the end points this line will again intersect on one point the line *A*—*A'* just at point *A'*. Namely, the point of intersection the situation of which indicates the composition of the system just lies on the MnO_2—Mn_3O_4 side of the triangle. In the case of these values the sample investigated has two constituents and its composition is:

20 per cent MnO_2 + 80 per cent Mn_3O_4

c) If on examining the sample after it has been heated no change in the active oxygen can be observed, $\triangle O = 0$ per cent, MnO_2 is not present, hence the system has two components and its composition is given by the point *A* of the *A*—*A'* line lying on the Mn_2O_3—Mn_3O_4 side of the triangle, i. e. the composition is:

71 per cent Mn_2O_3 + 29 per cent Mn_3O_4.

The above theoretical example illustrates the course of the determination. In the following a practical instance is given:

The analytical data of a manganite sample from Ilfeld are as follows:

	Sample of room temperature		Sample heated at 600° C	
	measured	calculated to 100 per cent	measured	calculated to 100 per cent
MnO	81,13	89,59	89,68	89,86
O	9,42	10,41	10,12	10,14

On the basis of the values obtained at the examination of the sample of ordinary temperature and recalculated to 100 per cent the composition on diagram N°. I. would be: 96,8 per cent Mn_2O_3 + 3,2 per cent MnO_2. On Fig. 2. point *X* indicates on the corresponding side of the triangle this composition.

However, a binary system of 70 per cent Mn_3O_4 + 30 per cent MnO_2 corresponds to the same MnO—O values which composition is given by *X'* on the corresponding side of the triangle. On the other hand, the points on the line *X*—*X'* give the composition of the ternary systems which are also possible at the measured MnO—O values.

Again only the value of $\triangle$ O per cent can decide the question. On the basis of the above data $\triangle$ O per cent = 0,27 per cent. If this value is plotted on to the ordinate and a parallel line drawn to the abscissa and the point of intersection of this line with the baseline of $\triangle$ O per cent projected on the abscissa and the corresponding distances measured on to the two sides of the triangle starting from the MnO_2 corner — as was mentioned in the above theoretical example — the line connecting the two end points (dotted blue line) will intersect the line *X*—*X'* at point *X*.

Thus as the point of intersection X lies on the MnO_2—Mn_2O_3 side of the triangle, the system contains these two components and its composition is: 96,8 per cent Mn_2O_3 + 3,2 per cent MnO_2. Hence the examined manganite is contaminated with 3,2 per cent pyrolusite.

If we want to check the exactness of the reading of the diagram the following must be taken into consideration: let us calculate on the basis of the composition read on the diagram the active oxygen content of the two possible systems the composition of which is given by points *X* and *X'*.

X

96,8 per cent Mn_2O_3 represents 9,81 per cent O

3,2 per cent MnO_2 represents 0,58 per cent O

X composition represents 10,39 per cent O

X'

70 per cent Mn_3O_4 represents	4,89 per cent O
30 per cent MnO_2 represents	5,52 per cent O
X' composition represents	10,41 per cent O; i. e. values are

obtained which are in good agreement with the result of the effective measuring (10,41 per cent O).

If on the other hand, the manganite also contains 3,2 per cent MnO_2 and is thus impurified with pyrolusite, in the case of it beeing heated at 600—700° C when this MnO_2 turns into Mn_2O_3, on the basis of calculation this conversion must be associated with a 0,26 per cent oxygen change. The estimated oxygen change is 0,27 per cent, i. e. the composition determined on the basis of the diagram actually corresponds to the real composition.

The exactness of the reading of the diagram can also be controlled on other simple examples. In one of his papers Dubois states that the dioxides having a composition of $MnO_{1,91}$—$MnO_{1,96}$ are definitely contaminated with Mn_2O_3, although the X-ray diagram only shows the dixiode lines. The data of a MnO_2 prepared by us recalculated to 100 per cent are as follows:

				Wt.%	Mol. props.	
MnO	82,18		Mn	63,71	1,1596	1
O	17,82	consequently	O	36,29	2,2676	1,95

i. e. the composition of our MnO_2 is precisely $MnO_{1,95}$. The measure of its contamination by Mn_2O_3 can readily established of the diagram I. of Fig. 2. The MnO_2 actually contains 93,2 per cent MnO_2 and 6,8 per cent Mn_2O_3.

The values of the used Mn_2O_3 recalculated to 100 per cent are: MnO = 89,78 per cent and O = 10,22 per cent, i. e. the determined values agree within the limits of error with the theoretical values. However, the MnO—O values — as can be seen on Table 2. — may also correspond to a system of a composition of 28 per cent MnO_2 + 72 per cent Mn_3O_4. On heating the sample at the temperature of 700° C neither a change of weight nor of the active oxygen could be observed. Thus it is proved that we are dealing with pure Mn_2O_3 and not with the theoretically also possible mixture.

From this MnO_2 contaminated to the extent established above and from pure Mn_2O_3 three mixtures were prepared. The MnO and O content recalculated to 100 per cent of the different mixtures is as follows:

	MnO Wt.%	O. Wt.%
a) 25 per cent MnO_2 + 75 per cent Mn_2O_3 =	87,90	12,10
b) 50 per cent MnO_2 + 50 per cent Mn_2O_3 =	86,01	13,99
c) 75 per cent MnO_2 + 25 per cent Mn_2O_3 =	84,10	15,90

On the basis of the above MnO—O values the real composition of the mixtures can be read on diagram I. of Fig. 2. If the MnO—O values are

calculated from the composition determined on the basis of the diagram the following data are obtained:

	MnO Wt.%	O. Wt.%
a) 23,4 per cent MnO_2 + 76,6 per cent Mn_2O_3 =	87,94	12,06
b) 46,6 per cent MnO_2 + 53,4 per cent Mn_2O_3 =	86,02	13,98
c) 70,0 per cent MnO_2 + 30,0 per cent Mn_2O_3 =	84,08	15,92

The above illustrate that the diagram does not distort. The MnO and O values calculated from the composition determined on the basis of the diagram are in good agreement with the corresponding values determined experimentally. Thus the exactness which can be achieved at the determination can be regarded as identical with the exactness of the applied chemical methods (the determination of the total manganese content according to Volhard-Wolff and the determination of the active oxygen with the oxalate method).

Further examinations are in progress to establish the exact composition if still a fourth component MnO (manganosite) is also present or if the substance also contains $MnCO_3$ (rodochrosite).

SUMMARY

In the case of MnO_2—Mn_2O_3—Mn_3O_4 systems the amount in per cent of the different constituents cannot be unequivocally determined on the basis of the MnO and O content only. The method elaborated by Classen is not either suitable for the determination of the composition of systems containing three components as it is only limited to the simultaneous determination of MnO_2 and Mn_2O_3.

Of the three oxides only MnO_2 undergoes a change giving off oxygen when it is heated at a temperature of 600—700° C and turns into Mn_2O_3. Hence by plotting graphically the following data: MnO, O and $\triangle O$ established by the chemical analysis the composition of any ternary system respectively that of any binary system which consists of any two of these three components can be exactly determined. The determination can also be carried out in the case of substances containing ferric iron, clay or other silicate minerals which occasionally contain the manganese oxides of higher valency mentioned above, only in slighter amounts.

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